

Infrared spectra of crystalline adipic acid and deuterated analogs

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(Received 10 August 1959)

Abstract—The infrared spectra of crystalline $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, $\text{DOOC}(\text{CH}_2)_4\text{COOD}$, $\text{HOOC}(\text{CD}_2)_4\text{COOH}$ and $\text{DOOC}(\text{CD}_2)_4\text{COOD}$ have been obtained in the 400 to 4000 cm^{-1} region. Deuteration shifts and polarization measurements are used to assign nineteen absorption bands of adipic acid to infrared active fundamental modes. The results of polarization measurements are related to the known structure of adipic acid. The band assignments are discussed in relation to the spectra of higher homologs. The bands observed in these compounds between 1180 and 1400 cm^{-1} probably arise from mixed B_u fundamentals involving carboxyl deformation, CH_2 wagging and CC stretching.

THE infrared spectra of crystalline high molecular weight carboxylic acids can be partially interpreted by applying symmetry considerations to certain parts of the molecules, such as dimerized carboxyl groups [1] and hydrocarbon side chains [2]. Some features of the spectra do not lend themselves easily to such treatment [2, 3]. The present study was undertaken to obtain a somewhat more detailed interpretation of the spectrum of a carboxylic acid of intermediate size, with the hope that some of the result can be carried over to related compounds of higher molecular weight. Adipic acid is suitable because its known molecular and crystal structure is closely related to a large number of heavier acids; partially and fully deuterated derivatives can be obtained; the molecule is small enough and possesses sufficient symmetry to permit a search for all expected infrared active fundamentals in the $400\text{--}4000\text{ cm}^{-1}$ region. Previous band assignments appear to have been fragmentary [1, 4–7] and in some cases contradictory. The fundamentals associated primarily with carboxyl dimers seem to be well established [1]. Polarization measurements have been limited to narrow regions [6] or seem to have been carried out without specifying the crystal orientation [4, 5].

Structural considerations

Crystalline adipic acid belongs to the space group C_{2h}^5 , with two molecules of C_i point symmetry in a unit cell. A detailed picture of the crystal structure as given by MORRISON and ROBERTSON [8] is shown in Fig. 1(A). The four central carbon atoms are coplanar, the carboxyl groups lie on a plane which is tilted about 6° to

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the plane of the carbon chain. For the purpose of identification and classification of infrared absorption bands it is convenient to regard the chains of hydrogen-bonded monomer units in first approximation as one-dimensional crystals [9, 10] with one adipic acid molecule as the repeating unit and the factor group of the one-dimensional space group isomorphous with C_i . Although the chains are slightly twisted [8], the segments consisting of $(CH_2)_4$ units and of hydrogen-bonded $(COOH)_2$ units are planar and it is still useful to classify the infrared active chain modes as

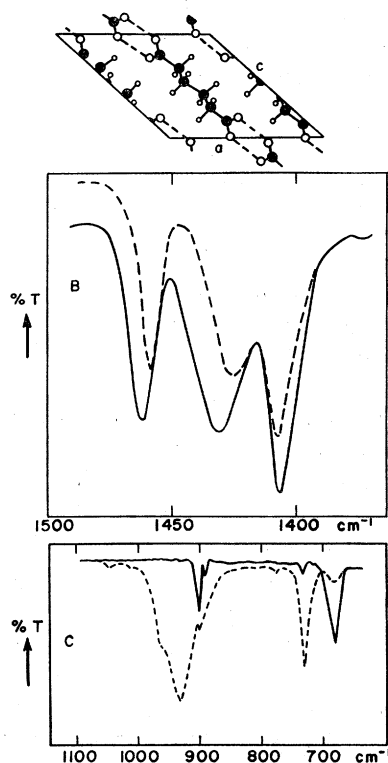


Fig. 1.

- A. Structure of adipic acid [8]. (O—H...O not shown).
 B. 1400–1500 cm^{-1} region. -- electric vector parallel to b . — electric vector perpendicular to b (within ab plane).
 C. 600–1100 cm^{-1} region. — electric vector parallel to c . --- electric vector perpendicular to c (within ac plane).

“in plane” (ip) and “out of plane” (op). If the slight periodic twist is neglected, (ip) and (op) correspond to B_u and A_u , respectively, permitting a comparison with a large number of related molecules and groupings with C_{2h} symmetry.

With one molecule of p atoms in the repeat unit, the number of observable fundamentals in the single chain approximation is $3p - 4$ [10], i.e. in the case of adipic acid fifty-six fundamentals of species $29A_g + 27A_u$. The twenty-seven

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infrared active A_u modes can be further subdivided into sixteen (*ip*) and eleven (*op*) modes on the basis of the pseudo C_{2h} symmetry. The approximate nature of the infrared active vibrations can be described by analogy with previous work on hydrocarbons [11, 12] and on carboxylic acids [1]. The (*op*) CC modes, the lowest (*ip*) CC mode and the modes involving primarily hydrogen bonds should occur below the investigated region [13, 14], leaving fourteen (*ip*) and seven (*op*) fundamentals to be accounted for. The presence of two molecules with C_i site symmetry in the C_{2h}^5 unit cell causes each single chain mode to split into an A_u and B_u branch, polarized along the b -axis and in a plane perpendicular to this axis, respectively [15]. The structure of the unit cell [8] suggests that (*op*) modes should have sizable A_u branches and B_u branches which are polarized roughly perpendicularly to the main axis of the chains (and to the c -axis of the crystal). Bands which have B_u branches approximately perpendicular to the c -axis are hereafter called "perpendicularly polarized". The polarization of (*ip*) modes depends upon the particular vibration involved. If the B_u branch is approximately parallel to c , the A_u branch should be very weak.

Experimental

Origin of samples and instrumentation

A purified and recrystallized commercial sample of adipic acid (Eastman Organic Chemicals)* was used. The sample of $\text{DOOC}(\text{CH}_2)_4\text{COOD}$ (d_2 compound) was prepared by hydrolyzing a deuterium oxide solution of disodium adipate with DCl, filtering and washing. Presence of a relatively small amount of residual OH groups was indicated by absorption in the 3000 cm^{-1} region. This might result in destruction of the C_i symmetry, rendering the spectra of this compound less significant than the spectra of the other acids. The fully deuterated acid (d_{10} compound) was obtained from Merck & Co., Ltd. (Montreal, Canada). No CH or OH stretching bands were noticeable, indicating high isotopic purity. $\text{HOOC}(\text{CD}_2)_4\text{COOH}$ (d_8 compound) was prepared by evaporating a 1% aqueous solution of the d_{10} compound to dryness. Neither characteristic CH nor OD bands were observed. All operations on carboxyl-deuterated samples were carried out under dry nitrogen.

The preparation of oriented samples has been described [2]. A Perkin-Elmer Model 21 instrument equipped with a NaCl prism and a AgCl polarizer was used in the $600\text{--}4000\text{ cm}^{-1}$ region. A Beckman IR-3 instrument equipped with KBr prisms and with LiF prisms was employed for the $400\text{--}600$ and $2000\text{--}4000$ regions, respectively. Because of experimental difficulties, no oriented samples were studied with the latter instrument. Polarization data are therefore available only for the region covered with NaCl prisms.

* Mention of specific products does not imply endorsement by the Department to the possible detriment of others not mentioned.

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Sample orientation and polarization measurements

The experimental problem of obtaining meaningful polarization data on molecular crystals with low symmetry has been discussed by NEWMAN and HALFORD [16] and by NEWMAN and BADGER [17]. For monoclinic crystals one eigenvector of the complex dielectric tensor (polarization axis) is symmetry fixed along the b axis, the others are unrestricted. Two crystal habits were observed for adipic acid samples prepared by the previously described method [2]: habit I with the ab planes, habit II with the ac planes parallel to the plane of the sample. The orientation and uniformity of each prepared sample was determined by investigation with a polarizing microscope and by establishing the crystalline plane of symmetry with the help of tilted samples [2]. A large number of experiments were necessary before samples with sufficiently uniform orientation were obtained. The final sample of habit I was used to measure spectra with the electric vector, ϵ , parallel to the ab plane, first parallel and then perpendicular to the symmetry fixed axis. Habit II was used to obtain spectra with ϵ perpendicular to the symmetry fixed axis, and parallel or perpendicular to c . To obtain an internal check, spectra with $\epsilon \perp$ and \parallel to c were also obtained on a tilted sample of habit I. The data were in good qualitative agreement with the spectra obtained with perpendicular incidence.

The quality of the observed results is illustrated in Fig. 1. Fig. 1(B) shows the 1400–1500 cm^{-1} region of adipic acid with $\epsilon \parallel$ and \perp to b (within the ab plane), Fig. 1(C) the 600–1100 cm^{-1} region with $\epsilon \parallel$ and \perp to c (within the ac plane). Fig. 1(C) shows that two out-of-plane modes which can be assigned with confidence (OH bending around 930 cm^{-1} and CH_2 rocking around 730 cm^{-1}) have no (or very weak) components along the c axis. A slight Christiansen effect [18] was observed on the band around 1200 cm^{-1} . Both the shape and apparent center of this band changed slightly ($\sim 5 \text{ cm}^{-1}$) when ϵ was rotated within the ac plane. For other bands the effect was very small.

Insufficient material was available to prepare well oriented deuterated samples. They tended to crystallize in habit II, with ac planes parallel to the sample plane. The frequencies listed in Table 2 were obtained on random samples observed with unpolarized radiation. The designations \parallel and \perp refer to measurements on the aforementioned partially-oriented samples.

Assignments

Table 1 gives the observed bands for adipic acid, their approximate intensity, polarization and assignment. Table 2 lists the assigned single chain fundamentals of the deuterated materials. A schematic correlation of the fundamentals of the light and deuterated materials below 1500 cm^{-1} is shown in Fig. 2. Survey spectra are shown in Fig. 3.

The six fundamentals associated with carboxyl groups are assigned in a straightforward way by comparison with the work of HADŽI and SHEPPARD [1]. The spectra of the d_8 and d_{10} compounds fully confirm the assignments of these

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authors. The only difficulty occurs in the 1300 cm^{-1} region of adipic acid, where probably three fundamentals lie very close to one another. The strongest A_u and B_u branches are assigned to the mixed OH bending, CO stretching fundamental.

Table 1. Infrared spectrum of adipic acid, 400–4000 cm^{-1}

cm^{-1}	<i>I</i>	Polarization	Assignment
3000*	s	$b, ac (\parallel)^{* \dagger}$	$B_u, A_u (ip)$ OH s [‡]
2963	m	$b, ac \perp$	$B_u, A_u (op)$ CH ₂ s
2953	m	$b, ac \perp$	$B_u, A_u (op)$ CH ₂ s
2925	w	b, ac	
2879	w	$b, ac (\perp)$	$B_u, A_u (ip)$ CH ₂ s
2650*	m	$b, ac (\parallel)$	
1710*	vs	b	$A_u \left. \begin{array}{l} B_u \end{array} \right\} (ip)$ C=O s
1695	vs	ac	
1463	m	ac	$B_u \left. \begin{array}{l} A_u \end{array} \right\} (ip)$ CH ₂ b
1460	m	b	
1433	m	$ac (\parallel)$	$B_u \left. \begin{array}{l} A_u \end{array} \right\} (ip)$ CO s (OH b)
1427	m	b	
1408	m	$b, ac (\perp)$	$B_u, A_u (ip)$ CH ₂ b
1357	w	$b, ac (\parallel)$	$B_u, A_u (ip)$ CH ₂ w
1315	w	$b, ac \perp$	$B_u, A_u (op)$ CH ₂ t
1300	m	$ac (\parallel)$	$B_u, (ip)$ CH ₂ w
1287	s	ac	$B_u (ip)$ OH b (CO s)
1287	m	b	$A_u, (ip)$ CH ₂ w
1272	s	b	$A_u (ip)$ OH b (CO s)
1254	w	b, ac	
1200	m	ac	$B_u \left. \begin{array}{l} A_u \end{array} \right\} (ip)$ CC
1194*	s	b	
1150	vw	$b, ac (\perp)$	
1044	vw	$b, ac \perp$	
965	sh	$b, ac \perp$	$B_u, A_u (op)$ CH ₂ r
932	s	$ac \perp$	$B_u \left. \begin{array}{l} A_u \end{array} \right\} (op)$ OH b
925	s	b	
902	m	$b, ac (\parallel)$	$B_u, A_u (ip)$ CC
890	w	$b, ac (\parallel)$	
787	vw	$b, ac \perp$	
736	m	$ac \perp$	$B_u \left. \begin{array}{l} A_u \end{array} \right\} (op)$ CH ₂ r
732	m	b	
687	m	$ac (\parallel)$	$B_u (ip)$ COO b
531	vw		
516	m		(ip) CC

* Approximate center of broad or very strong band.

† b , along monoclinic axis; ac , in the ac plane; \parallel, \perp , ac branch is approximately parallel or perpendicular to the c axis; $(\parallel), (\perp)$ the given component is somewhat stronger than the other.

‡ B_u, A_u refers to crystal symmetry; $(ip), (op)$ to molecular pseudo-symmetry. s, b, w, t, r, stretching, bending, wagging, twisting, rocking.

There are no corresponding difficulties in the deuterated samples. All bands assigned to (op) OH or OD bending modes show perpendicular polarization as predicted.

Three medium strength bands in the 1200 cm^{-1} , 800–900 cm^{-1} and 500 cm^{-1} regions, respectively, which are not appreciably affected by deuteration, are assigned to (*ip*) CC vibrations. The 1200 cm^{-1} region band has previously been assigned to the (*ip*) OH bending mode [5], but it has been pointed out that its persistence in the d_2 compound rules this assignment out [1]. The presence of a medium strength band around 1200 cm^{-1} in the d_8 and d_{10} compounds renders

Table 2. Infrared active fundamentals of deuterated adipic acids 400–4000 cm^{-1}

Description	Deuteration			$\nu(\text{H}_{10})/\nu(\text{D}_{10})$
	OD	(CD_2) ₄	Complete	
(<i>ip</i>) OH (OD) s	2260*	3000*	2270*	1.32
CH ₂ (CD_2) s	?	?	?	
CH ₂ (CD_2) s	2879	2117	2116 \perp	1.36
C=O s	1695*	1700*	1690*	1.00
CH ₂ (CD_2) b	1463	1086	1086 ()	1.35
CO s†	1352	1410 ()	1360	1.05
CH ₂ (CD_2) b	1409	1057	1045 ()	1.35
CH ₂ (CD_2) w	1375 ()	?	?	
CH ₂ (CD_2) w	1290 ()	958	958	1.35
OH (OD) b†	1057	1308	1069	1.20
CC	1200 ()	1180 ()	1185 ()	1.01
CC	868 ()	840 ()	813 ()	1.11
COO b	668 ()	664 ()	655 ()	1.05
CC	505	494	481	1.07
(<i>op</i>) CH ₂ (CD_2) s	2961 \perp	2236 \perp	2238 \perp	1.32
CH ₂ (CD_2) s	2951 \perp	2217 \perp	2220 \perp	1.33
CH ₂ (CD_2) t	1305 \perp	947 \perp	946 \perp	1.39
CH ₂ (CD_2) t	?	?	?	
OH (OD) b	690 \perp	921 \perp	680 \perp	1.37
CH ₂ (CD_2) r	910 \perp	713 \perp	718 \perp	1.34
CH ₂ (CD_2) r	740 \perp	560	557	1.32

Bands listed in order of occurrence in nondeuterated acid. Meaning of \perp , ||, s, b, w, t, r, same as in Table 1.

* Approximate center of broad or very strong band.

† Very approximate description. In OH compounds these modes are strongly mixed.

association with either OH or CH₂ groups unlikely. The frequency is somewhat higher than observed for infrared active CC modes in hydrocarbons [12]. However, ketones show a band in this region which has been assigned to a skeletal mode involving the CC bond next to the carbonyl group [19]. In adipic acid the band is probably due to a skeletal mode involving primarily the CC bond next to the carboxyl group.

The modes deduced from internal vibrations of CH₂ and CD₂ groups occur in the expected regions, although only three clearly distinguishable medium-strength

bands were observed in the stretching regions. The two higher bands, which show perpendicular polarization in all compounds, are assigned to the asymmetric CH_2 (CD_2) stretching modes by analogy with hydrocarbons, the third medium strength band to a symmetric stretching mode. The second (*op*) stretching mode appears either too weak or insufficiently resolved to be assigned with confidence. The CH_2 bending modes are very close to previously studied compounds with related structure [19].

The CH_2 and CD_2 modes of rotatory origin are still to be assigned. These modes, particularly the ones associated with wagging and twisting, are not easily identified

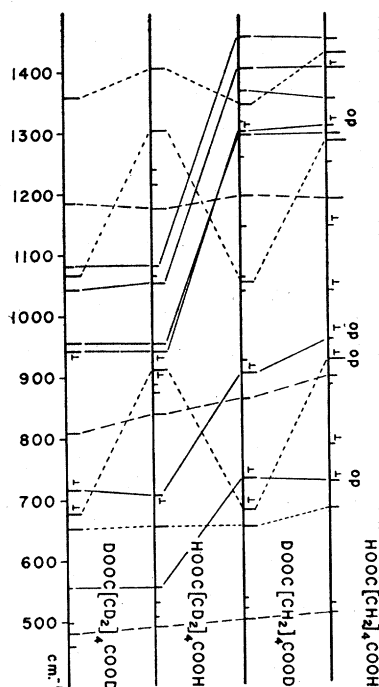


Fig. 2. Schematic presentation of the infrared spectra of light and deuterated adipic acids, 400–1500 cm^{-1} . *op*—out of plane vibrations. \perp —essentially perpendicular to the *c* axis. — modes associated with CH_2 (or CD_2) groups. --- modes associated with carbon skeleton. ····· modes associated with carboxyl groups.

in crystalline hydrocarbons [11, 12] and frequently show apparent frequency and intensity irregularities in alkyl halides and polymethylene halides [20–24], indicating a relatively strong sensitivity to intramolecular environment. The assignment of the CH_2 and CD_2 (*op*) rocking modes in the studied acids appears relatively reliable, although the higher frequency band in the nondeuterated compound is masked by

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[24] J. T. NEU and W. D. GWINN, *J. Chem. Phys.* **18**, 1642 (1950).

the strong (*op*) OH bending mode. All bands assigned to rocking modes which occur in the NaCl region showed perpendicular polarization, as expected (the polarization of the low frequency bands of the d_8 and d_{10} samples could not be measured with available instrumentation). In the CH_2 (*op*) twisting and (*ip*) wagging region [12] adipic acid has three unassigned weak to medium bands. The band at 1315 cm^{-1} is perpendicularly polarized and is on that basis assigned to a twisting mode. The other two which show $\parallel > \perp$ polarization are assigned to the two wagging modes. The d_8 and d_{10} compounds have only two bands of appreciable intensity in the region where CD_2 wagging and twisting modes should occur. The

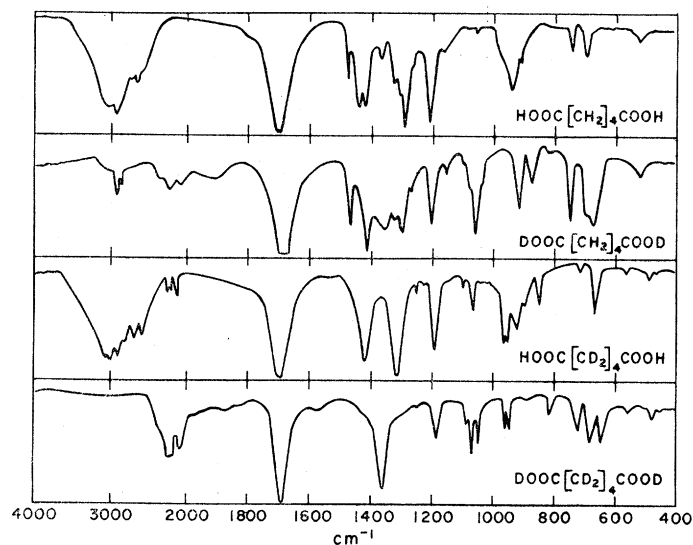


Fig. 3. Observed survey spectra.

higher band with $\parallel > \perp$ polarization is assigned to a wagging mode, the lower, perpendicular band, to a twisting mode. Although some very weak bands occur which could be taken as the missing fundamentals, such assignment would be somewhat arbitrary.

Some weak remaining bands must arise from combinations. Their assignment is presently not possible because low-frequency modes and Raman-active modes have not been studied.

Discussion of the results

Nineteen out of the twenty-one expected infrared-active fundamental modes of adipic acid could be assigned to observed bands on the basis of deuteration shifts and the assumption that (*op*) modes are perpendicularly polarized in the sense defined in earlier sections. The assignments appear reasonably reliable, with the possible exception of some CH_2 and CD_2 modes of rotatory origin. The (*ip*) OH bending and C—O stretching modes are strongly coupled [1], while the shifts in CH_2 modes upon deuteration are close to $2^{-1/2}$. One skeletal mode appears at somewhat higher

frequencies than in hydrocarbons. The polarization of (*op*) modes indicates that the approximation adopted for these modes is valid. The polarization of (*ip*) modes within the *ac* plane did not always show an obvious dependence on the direction of the chemical bond primarily involved. Thus, in the nondeuterated acid, the lower CH₂ bending mode is 1, the higher one ill-defined. In the *d*₂ and *d*₈ compounds both are ill-defined, whereas in the *d*₁₀ compound they appear more parallel than perpendicular. The effect seems to be larger than could be explained by optical phenomena alone. It appears that any conclusions drawn from the polarization of modes which are not fixed by molecular symmetry (or, as in this case, pseudo symmetry) must be taken with caution, even if the mode can be called "separable" by frequency considerations.

Our instrumentation and techniques were not accurate enough to determine with precision splittings due to intermolecular forces. The results obtained on the nondeuterated acid showed the presence of such splittings for many observed fundamentals. The polarization of the two branches of the CH₂ rocking mode around 730 cm⁻¹ and the bending mode around 1460 cm⁻¹ is the same as in monoclinic *n*-C₃₆H₇₄ [25], but the amount of splitting is smaller, indicating weaker forces between CH₂ groups of different chains, as expected from the structure [8].

The region roughly between 1180 and 1360 cm⁻¹ deserves attention because of its relationship to the spectra of higher homologs of adipic acid, which have been studied by CORISH and DAVISON [7]. The data obtained in the course of this work indicate that two (*ip*) CH₂ wagging modes, one (*ip*) carboxyl mode and one (*ip*) skeletal mode absorb in this relatively narrow region. For the higher even numbered homologs, which probably are very nearly planar [26], (resulting in molecular symmetry *C*_{2h}) one wagging mode is added for every two CH₂ units. The increasing number of bands with considerable intensity which occur between 1180 and 1360 cm⁻¹ can thus be regarded as arising from somewhat mixed molecular *B_u* fundamentals involving carboxyl deformation, CH₂ wagging and CC stretching. Similar considerations might apply to straight chain monocarboxylic acids [2, 3, 27] with the distinction that the presence of a skeletal mode in this region has not been established.

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